

GOVERNMENT OF JAPAN

Patent Office

KOKAI PATENT GAZETTE

(11) Disclosure No.: Sho 52-119697

(43) Disclosure Date: October 7, 1977

(51) Int. Cl. ²	ID No.	(52) Japan Class.	Intra-Office No.
C 08 G 18/14		26(5) G 121.3	6779-45
C 08 L 75/04 //		25(1) D 52	7160-45
(C 08 L 75/04		25(1) D 7	6474-45
C 08 L 63/00)			

Number of Inventions: 1 Examination Requested: No (Total of 4 pages)

(54) Title of Invention: Method of Forming Foams from Polyurethane Emulsions

(21) Application No.: Sho 51-36086

(22) Application Date: April 2, 1976

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SPECIFICATION

1. Title of the Invention

Method of Forming Foams from Polyurethane Emulsions

2. Claim

A method of forming highly impact-resilient foams characterized by adding a water-soluble or water-dispersible epoxy resin and a curing agent thereof when forming a foam by mechanically foaming a polyurethane emulsion.

3. Detailed Description of the Invention

The present invention relates to a method of forming foams having high impact resilience from polyurethane emulsions.

In the past, foams made using a synthetic polymer-based emulsion such as polyacrylate emulsion and styrene-butadiene copolymer emulsion or natural rubber latex as the starting material have been produced by various methods and are used for manufacturing materials, bedding, and the like. However, these are often inferior in such performance as mechanical strength, weathering resistance, laundering resistance, and solvent resistance, and for these to become suitable for still broader applications, for example, clothing uses, these points must be improved. On the other hand, foams obtained by mechanically foaming polyurethane emulsions are attracting attention from various directions lately because they have high performance that compensates for the above-mentioned drawbacks. However, forming a foam having good impact resilience while still retaining the soft feel that is characteristic of polyurethane was difficult by the methods of mechanically foaming polyurethane emulsions carried out in the past, so it has not yet led to a discovery of expanded applications. To become suitable for clothing applications in particular, improvement of this point was regarded as necessary.

As a result of various studies to improve this point, the present inventors discovered that by adding a water-soluble or water-dispersible epoxy resin and a curing agent of that when forming a foam by mechanically foaming polyurethane emulsions, a foam having high impact

resilience is obtained. That is, by also adding a water-soluble or water-dispersible epoxy resin and a curing agent thereof in addition to a foaming assistant and viscosity modifier to the polyurethane emulsion, mechanically foaming this by stirring, and then drying it, a foam having high impact resilience while regaining a soft feel and also having excellent solvent resistance, laundering resistance, weathering resistance, and mechanical strength can be obtained.

The polyurethane emulsion (A) employed when practicing this invention is not particularly limited, and various ones can be used. For example, it can be produced by (I) the method of dispersing a urethane polymer in water using a surfactant or (II) the method of introducing hydrophilic groups into the polyurethane molecules to make dispersion in water easy.

As the water-soluble or water-dispersible epoxy resin (B), polyglycidyl ether compounds of the aliphatic polyol type that are water-soluble or disperse relatively easily in water, such as glycerol polyglycidyl ether, ethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, and pentaerythritol polyglycidyl ether, epoxy resin emulsions made from epoxy dispersed in water using anionic or nonionic active agents, and also polyglycidyl esters produced from aliphatic carboxylic acids and epichlorohydrin can be mentioned.

As curing agents (C) that can react with and cure these epoxy resins, polyamines such as ethylenediamine, tetraethylenepentamine, triethylenetetramine, diethylaminopropylamine, and 2,4,6-tris(dimethylaminomethyl)phenol; polyamides that are the reaction products of a dimer acid and a polyamine such as ethylenediamine or diethylenetriamine; modified aliphatic amines obtained by modifying a polyamine by adding a mono- or diepoxy compound; and also salts of polyamines and polyamides such as carbonate of tetraethylenepentamine and hexamethylenediamine carbamate can be mentioned.

The appropriate loading of these water-soluble or water-dispersible epoxy resins (B) and their curing agents (C) is 1.5 to 2.5 parts by total weight of (B) and (C) per 100 parts of polyurethane emulsion (A). As for the addition ratio of (B) and (C), it is preferred to compound them so that the ratio of epoxy equivalents in (B) to the equivalents of active hydrogen that can react with epoxy groups in (C) is $(B):(C) = 1:1.2$ to $1:1.5$.

As the foaming assistants added to the mixture of (A), (B), and (C), sodium laurate, coconut oil soap, sodium myristate, ammonium stearate, sodium palmitate, sodium oleate, sodium higher alcohol sulfates, sodium higher fatty acid amide alkylsulfonates, saponin, gelatin,

and casein can be mentioned.

As the viscosity regulators, casein, alginates, gum arabic, bentonite, clay, carboxylated methylcellulose, polyvinyl alcohol, polyvinylpyrrolidone copolymer, polyethylene oxide polymer, and polyacrylate emulsion can be used. The loading of these is usually 0.1 to 5 parts, preferably 0.5 to 3 parts. A viscosity of 1,000 to 5,000 cP is appropriate.

The foam can easily be colored by adding an anionic or nonionic water-dispersible pigment. In this case, one must be careful that the anionic or nonionic active agent in the water-dispersible pigment does not have an adverse effect on the foaming effect.

According to the method of this invention, the drying of the foam can be done at room temperature, but a good foam is formed in a short time by heat treatment. Even if dried by rapid heating at this time, no defects such as cracks, loss of bubbles, or decrease in thickness will occur at all in the foam. Therefore, one can start the heating and drying from a temperature above 100°C from the very beginning. By contrast, it was difficult to obtain a good foam by the conventional methods unless one started the evaporation of water from a low temperature.

Because the foam formed according to the method of this invention has high impact resilience while retaining the performance characteristic of urethane resins, such as soft feel, dry cleaning resistance, laundering resistance, and weatherability, it is especially ideal for fields of clothing such as expanded synthetic leathers and suede-finish leathers.

This invention will now be explained by specific examples.

“Parts” and “%” shown hereinafter are parts by weight and percent by weight.

Reference Example 1

35 parts of tolylene diisocyanate was mixed in 180 parts of polypropylene polyether diol (average molecular weight 1,800) and reacted at 80°C for 3 hr to obtain any isocyanate-terminated prepolymer. 100 parts of that was added to 106 parts of an aqueous solution containing 6 parts of polyoxyethylene nonylphenol ether (40 moles of ethylene oxide) and emulsified/dispersed with a homomixer. The urethane emulsion obtained had a solids content of 50.7% and a viscosity of 350 cP/20°C, and it was milk-white and nonionic.

Reference Example 2

35 parts of tolylene diisocyanate was mixed in 200 parts of polypropylene polyether diol (molecular weight 2,000) and reacted at 90°C for 4 hr to obtain isocyanate-terminated

prepolymer. To this was added 4.9 parts of 2,2-dihydroxymethylpropionic acid, and a NCO-terminated prepolymer containing carboxyl groups was obtained. 100 parts of this prepolymer (COOH content: 0.7%; NCO content: 3.2%) was added to 105 parts of a 0.7% aqueous NaOH solution and emulsified/dispersed with a homomixer. The urethane emulsion obtained had a solids content of 49.1% and viscosity of 420 cP/20°C, and it was milk-white and anionic.

Reference Example 3

51.7 parts of 4,4'-diphenylmethane diisocyanate were reacted in a mixture of 150 parts of polyester diol having an average molecular weight of 1,500, which was obtained from ethylene glycol and adipic acid, and 15 parts of polyethylene glycol having an average molecular weight of 1,000 was reacted at 95°C for 1 hr, and an isocyanate-terminated prepolymer was obtained. 100 parts of this prepolymer was added to 110 parts of an aqueous solution containing 5 parts of a propylene oxide-ethylene oxide copolymer system with the trade name F-88 (Asahi Denka Kogyo) and 3 parts of sodium dodecylbenzenesulfonate and emulsified/dispersed with a homomixer. This urethane emulsion had a solids content of 49.1% and a viscosity of 250 cP/20°C, and it was milk-white and anionic.

Practical Example 1

To 100 parts of the urethane emulsion of Reference Example 1 were added 5 parts of neopentyl glycol diglycidyl ether, which was produced from neopentyl glycol and epichlorohydrin, 2 parts of triethylenetetramine, 2.5 parts of a 10% aqueous solution of polyvinyl alcohol (degree of saponification: 78-81 mol%) as thickener, and also 4 parts of ammonium stearate as foaming assistant, and these were mixed until uniform. This mixture was stirred mechanically with a household hand mixer and foamed, producing fine, uniform bubbles. This foamed solution was cast on a glass plate with an applicator that adjusted it to a thickness of 10 mm, heat treated at 110°C for 7 min in a hot-air dryer, and a foamed sheet having fine, uniform bubbles and a good foamed state was obtained. Its physical properties are shown in Table 1.

Practical Example 2

To 100 parts of the urethane emulsion of Reference Example 2 were added 12 parts of a bisphenol A-type water-dispersible epoxy resin (solids content 45%), 3 parts of tetraethylene-pentamine, 2 parts of a 30% aqueous solution of polyvinylpyrrolidone copolymer as thickener, and 4 parts of a 20% aqueous solution of potassium oleate as foaming assistant, and these were

mixed until uniform. This mixture was treated as in Practical Example 1, and a foamed sheet was obtained. Its physical properties are shown in Table 1.

Practical Example 3

To 100 parts of the urethane emulsion of Reference Example 3 were added 9 parts of glycerol triglycidyl ether and 4 parts of polyamide (condensate of dimer acid and alkylene-polyamine; amine value 400), 1.5 part of a polyacrylate emulsion of the ammonia thickening type having the trade name Primer ASE-60 as thickener, 2 parts of a water-dispersible nonionic pigment (light brown; solids content 52%), and 5 parts of ammonium stearate as foaming assistant, and these were mixed until uniform. This mixture was treated as in Practical Example 1, and a foamed sheet was obtained. Its physical properties are shown in Table 1.

Table 1

	Addition of (B) + (C)	Impact resilience*	Feel**	Foamed state after drying ***
1. Practical Example 1	No	20 sec	Soft	Slight cracking
	Yes	1 sec	Soft	Good
2. Practical Example 2	No	25 sec	Soft	Thickness of foamed layer decreased
	Yes	0 sec	Soft	Good
3. Practical Example 3	No	15 sec	Soft	Cracking
	Yes	0 sec	Soft	Good
4. Melamine resin added instead of (B) + (C) as in Practical Example 1 (7 parts)****		0 sec	Extremely soft	Foamed layer decreased; cracking

* Indicates the time from causing a depression in the foamed sheet by pressing strongly with the fingertips from above, until the distortion returned to normal.

** The foamed sheet was judged by touch.

*** Dried with a hot-air dryer at 110°C for 7 min.

**** Sumitex Resin M3 (melamine resin produced by Sumitomo Chemical Industry KK) + promoter ACX

Hodogaya Chemical Industry K.K.